Comproportionation Reaction Synthesis to Realize High-Performance Water-Induced Metal-Oxide Thin-Film Transistors

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Solution-processed high-*k* dielectric and metal-oxide semiconductor thin films have been widely studied in low-power and flexible electronics. However, a high temperature required to form a condensed and uniform film limits their applications in printable, flexible, transparent and low-cost electronics. In this paper, a completely novel and environmental-friendly comproportionation reaction synthesis (CRS) is presented to obtain amorphous aluminum oxide (AlOx) thin films for solution-processed thin-film transistors employing water as the precursor solvent. Thermogravimetric measurement reveals that the thermal decomposition of CRS-AlOx precursor is completed at ~300 °C, which is 100 °C lower than that of the conventional water-induced AlOx. The morphological, optical, crystallization, compositional, and electrical properties of CRS-AlOx and conventional AlOx dielectric films are studied systematically. Meanwhile, water-induced In2O3 metal oxide semiconductor layers were formed on these dielectrics at low temperatures, and TFTs based on In2O3 and AlOx were formed and characterized. Compared with TFTs based on conventional AlOx showing low mobility and low clockwise hysteresis, In2O3 TFTs based on CRS-AlOx exhibit improved electrical performance and counterclockwise hysteresis in the transfer curves. In2O3 Water-induced TFTs fabricated on CRS-AlOx formed at a low temperature of 250 °C has average mobility of 98 cm2V-1s-1, while devices annealed on 300 °C and 350 °C show average enhanced mobilities of 123 cm2V-1s-1 and 128 cm2V-1s-1,respectively. Through detailed chemical composition characterization and electrical characterization, the high mobilities of TFTs based on CRS-AlOx dielectrics are correlated to trap states in CRS-AlOx, which resulted in a significantly increased electron concentration and counterclockwise hysteresis in the transfer curves.

1. Introduction

Metal-oxide thin-film transistors (MOTFTs) have attracted enormous attention for next-generation display applications such as large-area flexible electronics and printable displays.[1-3] Compared with traditional amorphous silicon TFTs and organic TFTs, they benefit from advantages including high mobility, superior optical transparency, good uniformity, and electrical stability.[4-7] Vacuum-based techniques, like radio-frequency magnetron sputtering, atomic layer deposition (ALD), and low pressure chemical vapor deposition (LPCVD), are widely employed to fabricate those MOTFTs.[7, 8] However, high-vacuum equipment is required for these techniques, which results in high fabrication costs.[8] For the production of large-area and cost-effective electronics, solution-based techniques have gained attention as the more competitive candidates owing to their simplicity, large-area uniformity, low-cost, and atmosphere manufacturing.[5, 6, 9] The studies on solution-processed MOTFTs have been identified and developed because metal-oxide thin films could be simply deposited from solution precursors by using solution-based methods such as screen printing, spin-coating, inkjet printing, and spray pyrolysis.[10-13] By combining a high-*k* dielectric layer with a metal–oxide active layer, superior TFT electrical performance can be obtained via the solution process, reducing the operating voltage and the threshold voltage. Additionally, higher channel mobility can be obtained by employing a high-*k* gate insulator to induce a strong interfacial carrier accumulation from a high capacitance intensity, compared with a traditional SiO2 dielectric.[14] Various solution-processed inorganic dielectrics like aluminum oxide (Al2O3), zirconium oxide (ZrO2), hafnium oxide (HfO2) and their mixtures have been studied in previous reports.[8, 15-17] However, the ideal performance of these high-*k* materials generally requires high annealing temperatures over 400 ℃ within the fabrication process.[18]

In order to address this challenge, innovative techniques, including solution combustion synthesis, UV/Ozone (UVO) treatment and deep ultraviolet (DUV) treatment have been developed accordingly to deposit high-quality metal oxide semiconductor and high-*k* dielectric materials at relatively lower temperatures.[10, 19, 20] However, either DUV or UVO methods requires additional post-treatments to form high-quality thin films for TFT applications. Whereas, in terms of the solution combustion synthesis method, the fabrication of high-performance thin films based on combustion reaction can be facilitated simply by a simple annealing process at atmospheric conditions. The essence of the combustion synthesis method is to involve an oxidizer (nitrates) and a fuel like urea or acetylacetone into an organic and toxic 2-methoxyethanol (2-Me) precursor solvent.[8, 19] During the annealing step, an exothermic combustion reaction occurs, supplying external heat to the thin film. As a result, the external heat for the removal of residual solvents, film formation, and densification is reduced accordingly. A major challenge to this novel technique is adjusting the chemical composition of the precursor, oxidizer, additive fuel and the condition to induce an efficient exothermic reaction.[21] Another important issue in toxic 2-Me is widely used as the solvent for combustion precursors, whereas the employment of eco-friendly fabrication process is hence required.

**Table 1** summarized high mobility solution-processed MOTFTs with solution-processed high-*k* dielectrics containing hysteresis information in transfer characteristics. To achieve high-mobility (>40 cm2V-1s-1) fully solution-processed TFTs, relative higher hysteresis (>1 V) in transfer curves is inevitable in nearly all reported literature. This phenomenon can be explained by several mechanisms related to defect states and traps in solution-proposed high-*k* dielectrics. A mobility enhancement model was found attributed to the presence of donor-like electron traps in solution-processed high-*k* ZrO2 insulators.[22] Other studies also reported mobility enhancement and counterclockwise hysteresis based on solution-processed high-*k* dielectrics as a possible consequence of absorbed water.[23, 24] In their study, mobility enhancement over 100 cm2V-1s-1 is observed along with a large counterclockwise hysteresis (ΔV>2 V).

In the present study, we suggest a novel solution combustion method to synthesize solution-processed high-*k* dielectrics by using comproportionation reaction synthesis at low temperatures. A systematic investigation was conducted to reveal the effect of comproportionation reaction on the physical and chemical characteristics of water-induced CRS-AlOx. Based on the low-temperature processed CRS-AlOx dielectrics, water-induced In2O3 TFTs were fabricated respectively. The fully water-induced TFTs exhibited high mobilities over 100 cm2V-1s-1with relative lower counterclockwise hysteresis (∆V<0.3 V). In addition, an in-depth study was conducted to further determine the mechanism between high mobilities and the counterclockwise hysteresis in the transfer curves. Despite solution-processed TFTs with high mobilities could be achieved by involving defect states or water in the dielectrics, relatively higher hysteresis (∆V >1 V) was ineluctably accomplished in previous studies.[23-26] Hereon, our approach presented low-hysteresis MOTFTs with high mobilities to be obtained at low temperatures by using eco-friendly and safe precursor solvents (deionized water).

2. Results and Discussion

2.1 Precursor solution preparation and characterization

Solution combustion synthesis of high-*k* dielectric and metal-oxide semiconductor thin films have been crucial for reducing the processing temperature of high-quality MOTFTs. The exothermic combustion reaction applied to solution-processed MOTFTs was proposed by Tobin J. Marks firstly.[19] By incorporating an oxidizer like nitrates or chlorides and an organic fuel like acetylacetone or urea, a violent redox reaction occurs. The localized exothermic redox reaction and massive reaction heat generated within the as-deposited film increase the local temperature inside the thin film, which facilitates the decomposition of residual impurities and promotes the precursor conversion into the metal-oxide lattice. As a result, the requirement for external high thermal energy is avoided. Since 2011, various MOTFTs based on high-*k* dielectrics formed by solution combustion synthesis have been comprehensively reported.[8, 27, 28] However, toxic solvent 2-Me is widely used as the solvent for combustion synthesis and one of the challenges in this process is to induce an exothermic redox reaction without remaining any residual organics due to insufficient decomposition of fuel.

The fabrication process and proposed comproportionation reaction synthesis mechanism for AlOx high-*k* dielectrics are described in **Figure 1a**. It should be noted that none of the organic components was involved in the CRS process. The solution comproportionation reaction synthesis of AlOx from aqueous Al2(NO3)3 precursor solution and ammonia gas could be represented by the combination of aluminum nitrate hydrolysis process and comproportionation reaction. By spin-coating the Al2(NO3)3 precursor solution in NH3/Air atmosphere condition, ammonia dissolves into the aqueous precursor solution, followed by the formation of aluminum hydroxide and ammonium nitrate as a result of the reaction of ammonium hydroxide and aluminum nitrate.

(1)

For comparison, the simplified conversion process for a conventional solution-processed AlOx, from liquid precursor to dense AlOx thin film, could be represented as follows:

(2)

(3)

(4)

Compared with the CRS process, the anions derived from the conventional as-deposited gel are thermally decomposed by external heat and relatively high annealing temperature is needed to replace NO3-1with H2Oduring hydrolysis prior to the achievement of the dense and AlOx thin films.As the conversion of Al(NO3)3 into Al(OH)3 is partially completed during the deposition process in CRS process, the external heat to convert the as-deposited gel into the AlOx is thus reduced accordingly. During the low-temperature annealing process, an acute exothermic comproportionation reaction occurs, followed by the decomposition of aluminum hydroxide and the formation of the metal-oxide network. The theoretical reaction equation neglecting possible secondary reactions during the annealing process in CRS process can be represented as:

(5)

(6)

The overall reaction can thus be written as below:

(7)

To investigate the effect of comproportionation reaction on the thermal behavior of as-deposited AlOx, thermogravimetric and differential thermal analysis (TG-DTA) were performed and the results are shown in **Figure 1b**. For the thermal decomposition process of CRS-AlOx precursor, an abrupt mass loss at 250 °C is observed, which coincides well with the violent exothermic peak observed in the differential scanning calorimetry (DSC) curve. The broad exothermic peak confirms the occurrence of the comproportionation reaction and enabled the formation of AlOx at a relatively lower annealing temperature.[9] For comparison, no obvious exothermic peaks and abrupt weight loss are observed for the conventional water-induced AlOx precursor. TGA curve indicates that the minimum temperature needed for full degradation of CRS-AlOx precursor is ~300 °C, which is ~100 °C lower than that of the conventional precursor. This can be attributed to the exothermic heat confirmed by the DSC result, reducing the external heat required for the formation of metal-oxide framework, as shown in **Figure 1c**. The chemical compositions of as-deposited precursor gel were investigated by X-ray photoelectron spectroscopy (XPS) measurements in order to confirm the proposed mechanism shown in **Equation (1)**. All the XPS peaks were calibrated by taking C 1s reference at 284.7 eV to compensate the charge-induced shift. The Al 2p peaks and N 1s peaks for as-deposited conventional AlOx precursor gel and CRS-AlOx precursor gel are shown in **Figure 1d** and **Figure 1e**, respectively. The XPS result shows a single Al 2p peak in the case of conventional AlOx, whereas, shift to higher binding energy is observed for the CRS-AlOx precursor gel. The shift of the Al 2p peak to higher binding energy could be attributed to the increase of OH- ions in the film due to the formation of Al(OH)3.[29, 30] The N 1s peaks of the CRS-AlOx precursor gel shows an additional NH4+-related peak compared with the conventional aqueous AlOx precursor gel as a consequence of the production of the ammonium nitrate.

2.2 Dielectric Thin Film Characterization

Structural and morphological characterization of the dielectric thin films were investigated by atomic force microscopy (AFM) and x-ray diffraction (XRD), shown in **Figure 2a**, **Figure 2b,** and **Figure 2c**, respectively. Considering grain boundaries act as preferential paths for impurity diffusion and leakage current, which leads to poor dielectric performance, amorphous dielectric films are preferred for TFTs.[6, 8] In addition, the amorphous film presents smoother surface than crystalline one, with which dielectric/semiconductor interface properties can be improved. **Figure 2a** and **Figure 2b** show the AFM images of CRS-AlOx and conventional AlOx thin films annealed at 300 °C. The AlOx fabricated by the comproportionation reaction synthesis has a smaller RMS value compared with the conventional one. This is because that the conversion of Al(NO3) solution into insoluble Al(OH)3 is partially complicated during the spin-coating step in the CRS process, which provides for smaller volume loss during condensation and densification in annealing step and benefits to form highly dense and uniform films.[31] XRD patterns, shown in **Figure 2c**, indicate that the CRS-AlOx thin films are amorphous up to 350 °C, which coincides with previous reports.[32]

**Figure 2d, Figure 2e and Figure 2f** show the leakage current-gate voltage (*I-V*), the capacitance-frequency (*C-f*) characteristics, and detailed areal capacitance values measured at different frequency conditions along with thickness data for metal-insulator-metal (MIM) devices, respectively. It is clearly seen that the leakage current density of the CRS-AlOx thin films decreases as the annealing temperature increases since the nitrate and hydroxyl residuals potentially leading to the conduction path decompose at high temperatures.[32] It is also noted that the leakage current density is improved by introducing the CRS process due to the exothermic reaction accelerating the formation of the metal-oxide frameworks.[21] The capacitance-frequency curves of MIM devices are shown in **Figure 2e** between 1 kHz-1 MHz. The CRS-AlOx films formed at 250 °C exhibits anomalous capacitance and dissipation factors because of the residual nitrates and hydroxides.[24, 30, 33]

2.3 Water-Induced In2O3 TFTs

Fully water-induced MOTFTs were formed by depositing water-based In2O3 precursor on CRS-AlOx, as demonstrated in **Figure 3a**. Here, precursor solutions for both dielectric layer and semiconductor were based on water. Compared with precursors based on toxic organic solvents such as 2-Me, impurity-free water-based precursors used in this work could achieve thin films with higher qualities since they have no organic residual to be removed within the process. In addition, we also demonstrated a novel solution combustion method to synthesize solution-processed high-*k* dielectrics by using comproportionation reaction synthesis (CRS) at low temperatures without using any organic fuel or oxidizer. This approach thus realized the combustion of the precursor without additional organic fuel to achieve high-quality high-*k* dielectric thin film with no organic residual. **Figure 3b** shows the optical transmittance of CRS-AlOx and In2O3/CRS-AlOx thin films. The results clearly demonstrated high optical transmittance for water-induced CRS-AlOx (>95%) and In2O3/CRS-AlOx (>90%) thin films on potential application towards transparent electronics.

The transfer and output characteristics of In2O3 TFTs were performed by measuring the devices based on dielectrics formed at different conditions, in a dark ambient atmosphere. The transfer characteristics of In2O3 TFTs fabricated on CRS-AlOx annealed at 250 °C, 300 °C, and 350 °C, and conventional AlOx annealed at 300 °C are shown in **Figure 4a**, **Figure 4b**, **Figure 4c**, and **Figure 4d**, respectively. Areal capacitance values measured at 100 Hz frequency were used in all mobility calculations in order to reduce the mobility overestimation in the calculation by using under-estimated steady-state capacitance. The In2O3 TFT with CRS-AlOx annealed at 250 °C shows a relative lower mobility of 105 cm2V-1s-1compared with those annealed at 300 °C and 350 °C partially due to the existence of residual groups and CRS reaction by-products suppressing carrier transport, considering the violent exothermic peak is around 250 °C and fully completed around 300 °C according to the TGA-DSC results.[32] The device annealed at 300 °C exhibits mobility of 129 cm2V-1s-1, a subthreshold swing of 0.17 V/decade, a threshold voltage of -0.4 V and an on/off current ratio ~105 respectively. The device annealed at 350 °C achieves similar mobility of 135 cm2V-1s-1­compared with the one annealed at 300 °C since the decomposition of the CRS precursor solution is completed at ~300 °C according to TGA-DSC results. High off-currents were also observed for In2O3 TFTs based on both CRS-AlOx and conventional AlOx attributed to the high carrier concentration and poor control of defects in this kind of solution-processed In2O3 result in large off currents [34-37]. A high on/off current ratio could be achieved by controlling the carrier concentration of the In2O3 through the addition of cations such as Zn2+, Dy3+, Y3+, Ga3+, Gd3+, Nd3+, and Mg2+ according to previous reports. [36, 38-42] It is worth noting that mobilities over 100 cm2V-1s-1 were derived for all of the devices on CRS-AlOx and could be possibly overestimated due to the underestimation of the areal capacitance used for mobility derivation (100 Hz as often used in the literature) and frequency dispersion in C-F characteristics.[43, 44] Several studies have shown MOTFTs based on solution-processed high-*k* dielectrics with high mobilities over 100 cm2V-1s-1 using capacitance measured at high frequency. T. B. Daunis reported a solution-processed TFT with mobility of 160 cm2V-1s-1 with a Ci at 10 kHz.[45] Y. Xu reported a ZnInSnO TFT with mobility of 117 cm2V-1s-1 and P. K. Nayak presented an In2O3 TFT with mobility of 127 cm2V-1s-1 both using capacitance measured at 1 MHz.[30, 46] The capacitance used for the mobility derivation may result in the overestimation of mobility values as a result of the frequency dispersion. Thus, in order to minimize the mobility overestimation attributed to the underestimated capacitance value, Agilent B1500A was employed to perform the quasi-static (QS) capacitance measurement with an integration time of 1 s for all the CRS-AlOx MIM devices. The quasi-static areal capacitances were calibrated to higher values of 123 nF/cm2 (k=8.7), 140 nF/cm2 (k=10.3), and 268 nF/cm2 (k=21.1) for CRS-AlOx annealed at 350 °C, 300 °C, and 250 °C, respectively. The mobility values were reduced to 128 cm2V-1s-1, 123 cm2V-1s-1, and 98 cm2V-1s-1 for TFTs based on CRS-AlOx annealed at 350 °C, 300 °C, and 250 °C, respectively. Although QS capacitance values were used for mobility derivation, the mobility is still relatively large, and it is interesting to note that the transistors on CRS-AlOx gate dielectrics exhibit counterclockwise hysteresis, which was commonly observed in high-mobility devices based on high-*k* dielectrics annealed at low temperature as summarized in Table. 1. Similar behavior and relationship between high mobility and hysteresis in solution-processed MOTFTs have been revealed and studied in a few previous reports. Intrinsic donor-like electron traps in solution-processed ZrO2 dielectrics could be responsible for the counterclockwise hysteresis and mobility enhancement because of the injection of electrons into the semiconductor by thermally activated emission from traps.[22] Daunis and Tran investigate water absorption as the origin of hysteresis and high mobility.[23] Electrons from defect states in solution-processed high-*k* dielectric could transfer to the gate electrode by applying positive gate voltage and positive charges remained in the dielectric, followed by an enhanced electric field through the dielectric, and thus a higher carrier concentration is induced within the active layer (within the semiconductor layer near dielectric). Because the channel current is enhanced mainly due to the increase in channel charge carrier concentration with positive gate bias and the channel current using the following equation in the saturation region is used to calculate the mobility, the calculated mobility is increased.

(8)

Here W, L, and Ci are the width and length of the channel, and capacitance per unit area of the gate insulator, respectively. Further careful analysis of the hysteresis in the transfer curve for **Figure 4a-c** was initiated as follows in the energy band diagram of **Figure 4e-g**. When the TFT based on CRS-AlOx dielectrics is initially biased with a gate sweep voltage from negative to positive, emission of electrons into the gate electrode from filled donor-like electron traps in CRS-AlOx is induced by the positive gate bias. As a consequence, the sweep-up gate bias results in unfilled electron traps with positive charges along with an enhanced electric field within the dielectric, and hence increase the steady-state carrier concentration in the In2O3 as shown in **Figure 4e-f**. After that, the TFT is biased with a gate voltage from positive to negative with remained positive charges/unfilled electron traps in the dielectric. The flat-band voltage shift due to the positive charge in the dielectric is then given by Gauss’s law:

(9)

where is the charge density per unit volume and d is the distance between the location of the charge and the oxide-semiconductor interface, as shown in **Figure 4e**. Since the positive charge is equivalent to an external positive gate bias, a more negative gate bias voltage is required to accomplish the same original semiconductor band bending, as depicted in **Figure 4g**. Thus, a negative voltage shift (counterclockwise hysteresis) is observed when the TFT is biased with the sweep-down gate voltage within the transfer characteristic. Due to the increased electron concentration in the channel as a result of the enhanced positive electric field, the TFTs based on CRS-AlOx could be hence operated at low operating voltages.

The transfer characteristics of In2O3 TFT fabricated on CRS-AlOx with low operating voltages of 0.5 V and 1 V and corresponding output characteristics are shown in **Figure S2** respectively.

2.4 TFT Gate Bias Stability Test

In order to further confirm increased electron concentration in the channel as a consequence of electron trap states in CRS-AlOx dielectric, positive, zero, negative gate bias stress measurements were performed, as demonstrated in **Figure 5a** and **Figure 5b**. Under negative or zero gate bias with increasing time, shown in **Figure 5a**, there are negligible changes in ID and Vth with time. In contrast, when the turn-on positive gate bias is applied, drain current increases with gate bias time and Vth has a negative shift, as shown in **Figure 5b**. It further confirms the presence of bias-induced positive charges in the CRS-AlOx dielectrics, since a more negative gate bias is required to achieve the same semiconductor band bending at the threshold voltage because the remained positive charge is equivalent to an added positive gate bias for the semiconductor. By applying a positive gate bias with an increasing time period, more electrons from defect states in the CRS-AlOx dielectric are transferred to the gate electrode, remaining more positive charges in the solution-processed dielectric (**Figure 5c**). For charge transfer from the filled electron states of the CRS-AlOx into the gate electrodes, the electron transfer time increases exponentially as the distance of the traps from the dielectric/gate interface gains.[23] Considering the assumption that defect states are located uniformly throughout the dielectric, the electric field along with the induced compensatory channel charges are hence expected to increase with time. This relationship between ID and gate bias time can be possibly explained by the mechanism shown in the following equation, which is coincident with a previous report by Daunis and Tran:[23]

(10)

where qv is the charge in the channel at positive gate bias VG and q0 is the charge in the channel at threshold voltage VT. Let , the previous equation could be derived as:

(11)

Since *k* and q0 are constants, a further derivation is presented as:

(12)

where t is the bias duration/time. The derived equation clearly shows that the variation in Id1/2can be a result of the change in log (t). A similar increased ID under positive gate bias was also observed in Daunis and Tran’s previous report. The absorbed water was possibly identified as the main source of these defect states in their solution-processed AlOx dielectrics by soaking the dielectrics in deionized (DI) water overnight.[23]

As summarized in **Table 1**, various high-mobility MOTFTs based on solution-processed high-*k* dielectrics obtained similar counterclockwise hysteresis in the transfer characteristics. A mobility enhancement mechanism caused by electron donation from the intrinsic traps in solution-processed ZrO2 gate dielectrics was introduced by Zeumault and Subramanian.[22] Park and Kim revealed that nitrate ions in the solution-processed Al2O3 film facilitated the absorption of water molecules, which lead to high capacitance and high mobility.[24] Daunis and Tran verified the defect states attributed to the absorbed water in the insulator was responsible for the high mobility and hysteresis.[23] Among almost all previous literature on high-performance solution-processed In2O3 including reported hysteresis information, a remarkably large hysteresis was observed and toxic solvent 2-Me was employed as well. It is further worthwhile that, in our paper, fully water-induced In2O3 TFTs with high electrical performance were demonstrated with minimized counterclockwise hysteresis, which has been already confirmed in the summarized comparison in **Table 1**.

2.5 Source of Counterclockwise Hysteresis/Mobility Enhancement from CRS-AlOx Dielectric

To verify the source of the counterclockwise hysteresis and mobility enhancement in the transfer curves of our TFTs based on CRS-AlOx, we investigated the Fourier Transform Infra-Red (FTIR) shown in **Figure 5d.** Although the CRS reaction results in a low completed conversion temperature for the precursor, multiple broad peaks (2700 – 3800 cm-1) related to hydroxyl (OH) groups are still found for the CRS-AlOx precursors annealed at 250 - 350 °C. To further investigate the effects of the CRS reaction and identify the variation of the chemical states of the thin films at different annealing temperatures, XPS was performed on the conventional AlOx and CRS-AlOx thin films annealed at 250 °C, 300 °C, and 350 °C. The XPS O 1 s peaks of the conventional AlOx, and CRS-AlOx thin films annealed at 250 °C, 300 °C, and 350 °C are shown in **Figure 5e-h,** respectively. They can be deconvoluted into three peaks corresponding to the Al-O lattice oxygen centered at ~531.3 eV, AlO(OH) component centered at ~530.4 eV, and bonded oxygen such as oxygen vacancies or OH- centered at ~532.5 eV.[29]

For CRS-AlOx, XPS results revealed an increasing Al-O ratio of 46%, 54%, and 58% for CRS-AlOx annealing temperature increased from 250 °C to 350 °C. Considering the CRS reaction exothermic peak at around 250°C and the conversion is completed at around 300 °C, the increased Al-O ratio could be attributed to the formation of the metal-oxide framework and the decomposition of nitrate-related groups at low temperature as a result of the CRS reaction.[21]

Compared with the conventional AlOx, the XPS results confirmed lower AlO(OH) components and higher Al-O ratios in all of the CRS-AlOx thin films indicating higher densification of the metal-oxide frameworkas the result of the decomposition of the conventional AlOx thin film being not completely achieved at 300 °C and the effects of CRS reactions. Additionally, more OH groups compared with conventional AlOx thin films were found for CRS-AlOx thin films, which could be mainly responsible for these filled electron trap states in the CRS-AlOx dielectric, which contribute to mobility enhancement towards solution-processed metal-oxide TFTs. However, TFT with similar high-performance and hysteresis usually exhibits unreasonably large mobility based on solution-processed dielectrics at low temperatures, while our devices exhibit increasing mobility value with the increase of annealing temperatures. J. H. Park demonstrated Li-ZnO TFTs based on solution-processed AlOx with counterclockwise hysteresis and mobility of 47 cm2V-1s-1 at 350 °C. The mobility was reduced to 3.4 cm2V-1s-1 when 500 °C-AlOx was employed. P. K. Nayak reported a solution-processed MOTFT with a mobility of 82 cm2V-1s-1 (Ci at 1MHz) based on 250 °C-Al2O3 and increased mobility of 127 cm2V-1s-1 (Ci at 1MHz) based on 350 °C-Al2O3. (no transfer curve hysteresis information was given in this study)[30]. However, when a relatively high annealing temperature 500 °C was applied on the dielectric, there was a remarkably reduced mobility of 5 cm2V-1s-1 attributed to the reduced OH group concentration. A. Zeumault demonstrated high-mobility ZnO TFT based on solution-processed ZrO2 at 300 °C, while 400 °C-device showed lower mobility with counterclockwise hysteresis, and the 500 °C-device showed much lower mobility with clockwise hysteresis.[22] X. Liang also reported a transistor based on solution-processed 300 °C-Al2O3 with a higher on-state current and counterclockwise hysteresis compared with the one annealed at 400 °C showing negligible hysteresis.[47] For our devices, 300 °C and 350 °C annealed TFTs showed improved mobilities compared with 250 °C-TFT. Considering the violent exothermic peak is around 250 °C and the conversion was completed around 300 °C according to the TGA-DSC results, the lower mobility of 250 °C is mainly attributed to the nitrate residuals and reaction by-products as a result of the uncompleted CRS reaction. According to previous reports, it seems that high external energy by a relatively high annealing temperature (≥400 °C) is required to dramatically remove the intrinsic OH groups along with other residual, and thus reduce the counterclockwise hysteresis or transfer it into clockwise hysteresis. It is possibly to have TFTs with lower mobility and hysteresis when CRS-AlOx annealed at higher temperatures than 350 °C due to the dramatically reduced OH groups. However, in this work, the annealing temperature is up to 350 °C because a low annealing temperature is preferable for low-cost and flexible devices. The OH group ratio was found to be reduced slowly with the increase of annealing temperature, and was not fully removed at 350 °C. At annealing temperatures lower than 400 °C, the effects of increasing annealing temperature on the improved mobility could be possibly dominated by the decomposition of nitrate impurity and improved channel/dielectric interface, while maintaining a relatively higher portion of OH groups for mobility enhancement. For TFTs with solution-processed dielectrics annealed at low temperatures, lower hysteresis, and high mobility are not likely to be achieved at the same time. Our approach provides a low-temperature and facile route to obtain high-mobility MOTFTs with relatively lower/acceptable hysteresis for emerging low-cost and flexible devices in the future.

3. Conclusion

In summary, the comproportionation reaction synthesis process was successfully utilized to fabricate high-*k* AlOx dielectrics in low temperatures and their applications in fully water-induced MOTFTs were investigated accordingly. The CRS process enables the formation of high-quality CRS-AlOx at lower temperatures compared with the conventional aqueous route. The formation and properties of CRS-AlOx were analyzed by TG-DSC, XRD, AFM, ATR-FTIR, XPS, and typical electrical characterizations. It is confirmed that the thermal decomposition of CRS precursor solution and the formation of high-quality thin films are completed at ~300 °C, which is 100 °C lower than that of the conventional aqueous route. Additionally, the fully water-induced In2O3 TFTs were fabricated at low temperatures and exhibited superior electrical characteristics at low operating voltages. The relative higher mobility based on CRS-AlOx dielectrics could be mainly attributed to the donor-like trap states in the high-*k* dielectrics considering the existence of counterclockwise hysteresis in transfer characteristics and negative threshold voltage shift from positive voltage bias stability characterization. Chemical composition analysis including FTIR and XPS revealed that these trap states could be originated from the remained hydroxyl groups in the dielectrics. Comparing the reported TFT from previous literature with toxic 2-Me solvent in the precursor for the dielectrics and large hysteresis in transfer characteristics, our approach provides a novel environmentally friendly combustion route for the realization of high-performance mobility-enhanced water-induced MOTFTs with minimized hysteresis.

4. Experimental Section

*Precursor Solution Preparation*: The water-based AlOx precursor solution was obtained by dissolving 2.5 M aluminum nitrate nonahydrate (Al(NO3)3∙9H2O) into deionized (DI) water. For the In2O3 precursor solution, 0.15 M indium nitrate hydrate (In(NO3)∙H2O) was dissolved in deionized (DI) water. All the precursor solutions were stirred vigorously for 20 minutes and then ultrasonicated for 20 minutes. Before spin-coating, they had been filtered through a 0.45 µm polyethersulfone (PES) syringe filters.

*Fabrication and Characterization of Gate Dielectric Layers*: Prior to deposition all substrates, air plasma was performed on heavily doped silicon and quartz substrates for 30 minutes in order to enhance the hydrophilicity before spin-coating. For conventional aqueous AlOx thin films, the AlOx precursor solution was spin-coated in the air for 40s at 4500 rpm and annealed at 300 ℃ under ambient atmosphere for 1 h. The CRS-AlOx high-*k* dielectric layer was deposited by spin-coating the AlOx precursor solution in NH3/Air condition with indicated NH3 concentration (0.05 M – 0.2 M) and annealed at a selected temperature (250, 300 and 350 ℃) at ambient air for 1 h. The optimized ammonia gas concentration (0.05 M) was obtained by examing the surface morphology by optical microscopy, as shown in **Figure S1**. Thermal behavior characterization of precursors was carried by TG-DSC using a differential scanning calorimeter (TGA, Jupiter STA449F3) after dehydration at 105 °C for 12 hours. The samples were characterized in the air atmosphere up to 500 ℃ with a heating rate of 10 ℃/min and air gas flow of 60 sccm in an alumina crucible. The crystallization and structural information of the thin films were displayed using x-ray diffraction (XRD, BRUKER D8 ADVANCE) with Cu Kα radiation. The surface morphology of the thin films was investigated using atomic force microscopy (AFM, BRUKER Nanoscope V). Fourier Transform Infra-Red (FTIR) spectroscopy results of thin films formed on Si substrates were measured using an FTIR spectrometer (Agilent Cary 600). The chemical structure of the high-*k* dielectric thin films was measured by X-ray photoelectron spectroscopy (XPS, Kratos) using Al Kα radiation (1486.6 eV). The optical properties of thin films on quartz substrates were measured employing a UV/Vis by measuring transmittance (T) in the wavelength range of 200 - 800 nm.

*Electrical Device Fabrication and Characterization*: Metal-insulator-metal (MIM) devices were fabricated by simply spin-coating and annealing AlOx via conventional process or CRS process on to n-type heavily doped silicon substrates (<0.002 Ω·cm) as described above. Al top electrodes (150 nm thick) with an area of 0.07 mm2 deposited by electron beam evaporation via shadow mask on top of the dielectric layer, and unpatterned electrodes (100 nm) were deposited on the backside of the silicon substrates. The leakage current density measurements and capacitance-frequency and were carried out on the MIM devices by using an LCR meter (Agilent LCR meter 4284A) and a semiconductor device analyzer (Agilent B1500A Semiconductor Device Analyzer). The dielectric constants were calculated from the MIM capacitance value measured at 100 Hz. Ellipsometry was employed for measuring all of the film thicknesses.

Air plasma was performed on heavily doped n-type Si substrates, acting as the common gate electrodes, for 30 minutes in order to enhance the hydrophilicity before spin coating. The as-prepared CRS-AlOx and conventional AlOx films were deposited on heavily doped silicon substrates as described above. The In2O3 semiconductor films were deposited on the gate dielectric by spin-coating the In2O3 precursor solution at 3000 rpm for 20 s, followed an annealing process at 250 °C under ambient atmosphere for 30 minutes. Afterward, the Al drain and source electrodes were formed by electron beam evaporation through the shadow mask. The channel length (L) and width (W) were 75 µm and 1500 µm, respectively. Additionally, another layer of Al electrode was formed on the back side of the heavily doped silicon to reduce the dispersion caused by the parasitic effect.[48, 49] A W/L ratio of 20 could help to reduce the mobility overestimation efficiently according to previous reports.[32] The electrical characterization of the TFTs was done by using a semiconductor device analyzer (Agilent B1500A Semiconductor Device Analyzer). The field-effect mobility (*µ*SAT) of the TFTs was calculated as Equation (8). The subthreshold voltage swing (SS) is extracted by the following equation:

(13)

Gate bias stability stress measurements were performed on TFTs at ambient air condition. A constant gate bias voltage (-2 V, 0 V, and 2 V) was applied on TFT for indicated stress time.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Table 1.** Summary of fabrication and electrical performance of high-mobility solution-processed metal-oxide TFTs based on solution-processed high-*k* dielectrics.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Mobility  [cm2V-1s-1] | Channel/ Dielectric Materials | Channel/Dielectric Precursor Solvent a) | Channel/Dielectric Annealing Temp.  [°C] | Hysteresis in Transfer Curve | Ci/Frequency b)  [nFcm-2/Hz] | ∆V d)  [V] | REF c) |
| 129 to 123 | In2O3/AlOx | H2O/ H2O | 250/300 | Counter. | 133/100 to 140/QS | -0.2 | This work |
| 36 | In2O3/Al2O3 | H2O/ H2O | 250/250 | Clockwise | 47/100 | +5.0 | [50] |
| 40 | In2O3/Al2O3 | 2-Me/2-Me | 250/250 | Counter. | 200/1000 | -0.2 | [19] |
| 136 | In2O3/Al2O3 | H2O/EG and 2-Me | 250/250 | Counter. | 36/1000000 | -1.6 | [25] |
| 125 | In2O3/Al2O3 | 2-Me/2-Me | 250/250 | Counter. | 160/100 | -2.3 | [23] |
| 33 | ZTO/Al2O3 | AN & EG/ AN & EG | N/A/300 | Counter. | 80/10000 | -2.3 | [26] |
| 47 | Li-ZnO/Al2O3 | NH3·H2O/2-Me | 350/350 | Counter. | 144/20 | -1.4 | [24] |
| 20 | ZnO/ZrO2 | Methanol/2-Me | N/A/300 | Counter. | N/A | -0.4 | [22] |
| 31 | In2O3/Al2O3 | H2O/ H2O | 250/250 | Counter. | 136/100 | -0.35 | [32] |

a)(EG: Acetonitrile; AN: Ethyleneglycol; Counter.: Counterclockwise); b)(Ci/Frequency: Dielectric area capacitance and the frequency used in mobility calculation); c)(This table only summarized literature including hysteresis information in transfer characteristics. Most of the devices are composed of bottom gate and top contacts, using heavily doped silicon as gate and substrate); d)(The voltage shift (ΔV) reflecting the hysteresis was estimated and extracted approximately as the loop width at the medium of the transfer curves (ΔV between up and down gate voltages at the in the transfer curve) values for comparison with literature.).

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**Figure 1.** a) Schematic illustration of the comproportionation reaction synthesis process for the water-induced AlOx thin films. b) TGA curves of the CRS-AlOx and conventional AlOx precursors. The inset shows the corresponding DSC curves of the CRS-AlOx and conventional AlOx precursors. c) Energetics of the CRS process versus the conventional aqueous route. d) XPS spectra of Al 2p peaks for CRS-AlOx and conventional AlOx as-deposited precursor gel. e) XPS spectra of N 1s peaks for CRS-AlOx and conventional AlOx as-deposited precursor gel.



**Figure 2.** AFM images of a) the CRS-AlOx thin film annealed at 300 °C and b) the conventional AlOx thin film annealed at 300 °C. c) XRD spectra of the corresponding conventional AlOx thin film and CRS-AlOx thin films annealed at indicated temperatures. d) Leakage currents curves and e) Areal capacitance-frequency of conventional AlOx thin films and CRS-AlOx dielectrics thin films annealed at indicated temperatures. f) Areal capacitance values measured at 1k Hz, 100 Hz, and quasi-static conditions and thickness information for CRS-AlOx thin films annealed at indicated temperatures.



**Figure 3.** a) Eco-friendly fabrication steps of fully water-induced In2O3 TFTs based on CRS-AlOx dielectrics. b) Optical transparency of the AlOx, CRS-AlOx, and In2O3/CRS-AlOx thin films deposited on quartz substrates.

**Figure 4.** Representative transfer characteristics of the In2O3 TFTs fabricated on CRS-AlOx annealed at a) 250 °C, b) 300 °C, c) 350 °C, and d) Conventional AlOx annealed at 300 °C (VDS = 2 V). (e) Energy band diagram at the flat-band condition when the TFT is biased with a sweep-up gate bias voltage. (f) Energy band diagram showing electron transfer from filled electron defect states into the gate due to positive gate bias voltage. (g) Energy band diagram at the flat-band condition when the TFT is biased with a sweep-down gate bias voltage, inducing negative flat-band voltage shift (counterclockwise hysteresis).



**Figure 5.** a) Time-dependent variation in the transfer characteristics of In2O3 TFTs with CRS-AlOx dielectrics under negative 2 V gate bias. The inset shows the time dependence of normalized ID and Vth shift due to zero gate bias. b) Time-dependent variation in the transfer characteristics of In2O3 TFTs with CRS-AlOx dielectrics under positive 2 V gate bias. The inset shows the time dependence of normalized ID and Vth shift due to positive gate bias. c) Energy band diagram showing electron transfer from filled electron states in CRS-AlOx to the gate electrode under positive gate voltage and energy band diagram showing increased electron transfer from filled electron states in CRS-AlOx to the gate electrode under long-time positive gate bias. d) FTIR spectra for CRS-AlOx and conventional AlOx annealed at indicated temperatures. e) O 1s XPS spectra for conventional AlOx thin film annealed at 300 °C. O 1s XPS spectra for CRS-AlOx thin film annealed at f) 250 °C, g) 300 °C, and h) 350 °C.

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Supporting Information

Comproportionation Reaction Synthesis To Realize High-Performance Water-Induced Metal-Oxide Thin-Film Transistors

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**Figure S1.** Surface morphology of the as-deposited CRS-AlOx thin films annealed at 300 °C formed at corresponding ammonia concentration.



**Figure S2.** Representative transfer characteristics of the In2O3 TFTs fabricated on CRS-AlOx dielectrics annealed at 300 °C under a) 2 V b) 1 V, and c) 0.5 V operating voltages. Output characteristics of the In2O3 TFTs fabricated on CRS-AlOx annealed at 300 °C under e) 2 V f) 1 V, and g) 0.5 V operating voltages